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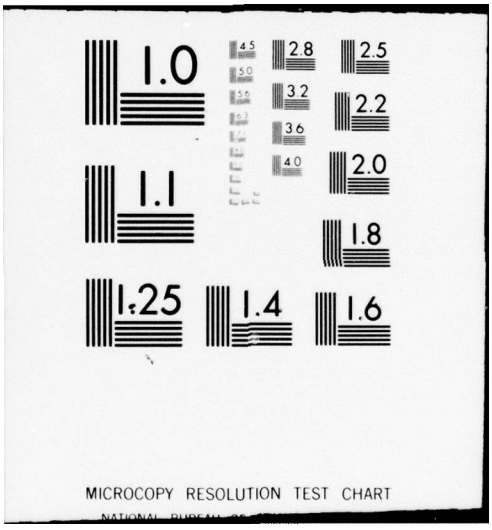
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Efficient Peroxyloxalate Chemiluminescence from Reactions of N-Trifluoromethylsulfonyl Oxamides with Hydrogen Peroxide and Fluorescers

by

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A new highly efficient class of chemiluminescent oxalic acid derivatives, N-trifluoromethyl sulfonyl oxamides, has been discovered. One member of this class, N,N'-bis(2,4,5-trichlorophenyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide, has given the highest chemiluminescence quantum yield (34%) reported for a chemiluminescent reaction in an organic solvent system.

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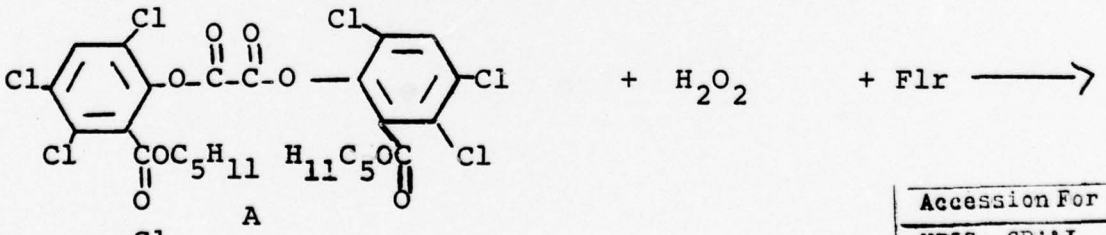
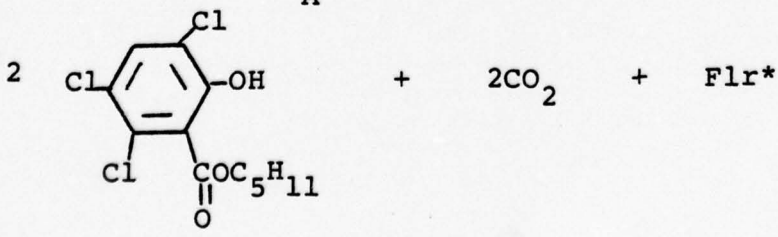
Efficient Peroxyloxalate Chemiluminescence from Reactions of N-Trifluoromethylsulfonyl Oxamides with Hydrogen Peroxide and Fluorescers[1]

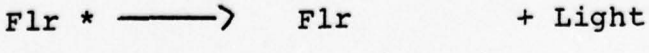
Shin-Shyong Tseng*, Arthur G. Mohan, Linda G. Haines, Lourdes S. Vizcarra, and Michael M. Rauhut.
Contributions from the Chemical Research Division, American Cyanamid Co., Bound Brook, N.J. 08805

Chemilumescence quantum yields above 0.11 ein. mole^{-1} (11%) from six N-trifluoromethylsulfonyl oxamides substituted on nitrogen by electronegatively substituted aryl groups. One compound, N,N-bis (trifluoromethylsulfonyl)-N,N'-bis(2,4,5-trichlorophenyl)oxamide, provided a chemiluminescent quantum yield of 34% making it the most efficient non-enzymatic compound known. Molecular sieves were found to be effective catalysts for the preparation of certain trifluoromethylsulfonamides from the amine and trifluoromethylsulfonyl chloride and for the preparation of the oxamides from oxalyl chloride and the sulfonamide.

Peroxyoxalate chemiluminescence[2] is illustrated by the reaction sequence outlined below:







Flr = a fluorescent compound

Chemiluminescence quantum yields of 0.10 to 0.18 ein. $mole^{-1}$ (10%-18%) have been reported for the oxalic ester A with fluorescers such as 9,10-bis(phenylethynyl)anthracene (green) and 1-chloro-9,10-bis(phenylethynyl)anthracene (yellow)[3,4]. Other oxalic esters such as bis(2,4,6-trichlorophenyl)oxalate[5,6], bis(2,4-dinitrophenyl) oxalate[5,7] and bis(3-trifluoromethyl-4-nitrophenyl) oxalate[5] have provided chemiluminescence quantum yields as high as 22 to 27%.

Other oxalic acid derivatives including mixed anhydrides[8], amides[8], sulfonamides[9] and oxalyl chloride[10] also provide chemiluminescence from this reaction, but are less efficient. In general, efficient peroxyoxalate chemiluminescence requires an oxalic acid derivative with an easily displaced leaving group[2]. In general, leaving groups containing electron attracting substituents have provided the highest efficiencies.

Results and Discussion

Inasmuch as the trifluoromethylsulfonyl (trifyl) group is one of the most powerful electron withdrawing groups known[11], we have investigated the chemiluminescence efficiency of a series of N-trifyl oxamides in the peroxyloxalate chemiluminescent system. The results, summarized in Table I, indicate that N-trifyloxamides which are further substituted on nitrogen by electronegatively substituted aromatic groups provide high chemiluminescence efficiency.

Indeed, the 2,4,5-trichloro compound 3 proved to be the most efficient non-enzymatic chemiluminescent compound yet discovered, with a chemiluminescent quantum yield of 34%.

The data in Table I indicate that increasing chlorine substitution on the aromatic ring of diphenyl triflyl oxamide generally provides a concurrent increase in chemiluminescence efficiency. However, the 2,4,6-trichloro derivative 4 was substantially less efficient than the 2,4,5-trichloro derivative 3, even though an ortho substituted chlorine is more electronegative than a meta[12]. As expected, substitution of aliphatic groups on the nitrogens of N-triflyl oxamide resulted in substantially reduced efficiency.

The general method for preparation of the triflyl oxamides involved treatment of the amine with triflic anhydride at

Scheme I

Synthesis of N-Trifyl Oxamides

$$RNH_2 + (CF_3SO_2)_2O \xrightarrow{(C_2H_5)_3N} RN(H)SO_2CF_3 + CF_3SO_3H$$

$$2RN(H)SO_2CF_3 + ClC(=O)C(=O)Cl \xrightarrow{(C_2H_5)_3N} RN(SO_2CF_3)C(=O)C(=O)N(SO_2CF_3)R + 2HCl$$

low temperature following procedures similar to those described by Hendrickson and Bergenson[13]. The acidic triflamides were then acylated with oxalyl chloride in the presence of triethyl amine to yield the desired trifyloxamides(Scheme I).

The presence of a labile chlorine atom in 2-chloroethyl trifluoromethylsulfonyl amide negated the use of triethylamine as the acid acceptor. In this case powdered 3A molecular sieves[14] effectively catalyzed the sulfonamide formation, while the use of "Proton Sponge"[R], 1,8-bis(dimethylamino)-naphthalene, a strong proton acceptor but a poor nucleophile[15] avoided displacement of the chlorine in reaction of the triflyamide with oxalyl chloride and afforded the oxamide in 80% crude yield. Molecular sieves were also effective catalysts for both the trifyl amide formation and the preparation of the oxamide 8. Trifylamides 4-chlorophenyl-trifluoromethylsulfonamide 1a, 2,4-dichlorophenyl-trifluoromethylsulfonamide 2a, 2,4,5-trichlorophenyl-trifluormethylsulfonamide 3a, and 4-nitrophenyl-trifluoromethyl sulfonamide 5a have been reported previously.[16]

Experimental Section

Melting points were taken on a "Mel-Temp" block and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer; samples were run in Nujol or in methylene chloride solutions. NMR spectra were recorded on a Varian Associates Model EM 360A spectrometer using tetramethylsilane as an internal standard. Mass spectra were recorded on a VG Micromass Model 7070F high resolution mass spectrometer attached to a VG Model 2035 data system, using electron impact (EI) mode or chemical ionization (CI) mode. In the CI mode, methane was used as the reagent gas. Microanalyses were performed by the Micro Analytical Laboratories of American Cyanamid Company, Bound Brook, N.J.

Determination of Chemiluminescence Quantum Yields

Absolute light measurements were made on a spectroradiometer-luminometer similar to that described by Roberts and Hirt[17] modified with a Janell-Ash model 82-410 grating monochromator and an RCA C31034 photomultiplier with a gallium arsenide photocathode operated at 1300 volts with dry ice cooling. Raw data was recorded digitally on a Hewlett-Packard 5150A thermal printer. Spectral response was corrected by calibration against a standard tungsten lamp. Absolute light intensities were obtained by deriving calibration constants based on the accepted fluorescence quantum yield (.55) for quinine sulfate[18] in .1N H_2SO_4 and by ferrioxalate actinometry[19] of the exciting light.

Chemiluminescence quantum yields in einsteins mole^{-1} of oxamides were calculated by monitoring the intensity decay at a single wavelength and calculating the intensity at each time interval in Einsteins sec^{-1} from the chemiluminescence spectrum. Chemiluminescence spectra were corrected for intensity decay. The total area under the decay curve was calculated using a combination of a Simpson's rule integration and an exponential extrapolation to infinite time[17]. Data was processed via a Digital Equipment Corp. PDP-1140 computer.

4-Chlorophenyl-trifluoromethylsulfonamide (1a) To a solution of 4-chloroaniline (5.12g, 0.04 mol) and triethylamine (4.04 g, 0.04 mol) in 60 mL of methylene chloride was added in portions 6.73 mL (0.04 mol) of trifluoromethanesulfonic anhydride at 0°C under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 hours. Evaporation of the solvent gave 10.2g of light brown oil, which solidified upon standing at room temperature. Recrystallization of the solid from cyclohexane gave 9.6g (93%) of pure 1a: m.p. 45-47°C; IR (CH_2Cl_2) 3300, 1360, 1200 and 1140 cm^{-1}; NMR ($CDCl_3$) δ7.2 (s, 1 NH) and 7.3 to 7.4 ppm (2 s, 4 aromatic protons); mass spectrum (EI), m/e 259 (M^+). Anal. Calcd for $C_7H_5NO_2SClF_3$: C, 32.43; H, 1.93; N, 5.41; S, 12.36; Cl, 13.51; F, 22.06. Found: C, 32.49; H, 1.80; N, 5.55; S, 12.21; Cl, 13.30; F, 21.79.

N,N'-bis(4-chlorophenyl)-N,N'-bis(trifluoromethylsulfonyl)oxamide (1)

Oxalyl chloride (0.5 mL; 0.056 mol) was added dropwise to a stirred solution of 1a (2.6g; 0.01 mol) and triethylamine (1.0g; 0.01 mol) in 20 mL of 1,2-dimethoxyethane at 0°C under a nitrogen atmosphere. The mixture was stirred at 0°C for 2 hours, heated to 60°C, held at 60°C for one hour; and evaporated to obtain a yellow solid which was treated with 20 mL of water. The solid which remained after the water extraction was collected and recrystallized from anhydrous ether to give 2.46g (85%) of white crystalline 1: mp 173-174°C; IR (Nujol) 1750, 1730, 1210 and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.30 to 7.65 ppm (m, aromatic protons); mass spectrum (EI), m/e 572 (M^+).

Anal. Calcd for $C_{16}H_8N_2O_6S_2Cl_2F_6$: C, 33.50; H, 1.40; N, 4.88; S, 11.17; Cl, 12.40; F, 19.90. Found: C, 33.51, H, 1.38; N, 4.74; S, 11.52; Cl, 12.10; F, 19.61.

N,N'-Bis(2,4-dichlorophenyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (2) The triflyl amide 2a was prepared by the procedure described for 1a using anhydrous ether as solvent affording 97% of crude product which after recrystallization from cyclohexane gave pure 2a: mp 84-86°C; IR (Nujol) 3250, 1360, 1200 and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.21 (s, 1NH) and 7.3 to 7.7 ppm (m, 3 aromatic protons); mass spectrum (EI), m/e 293 (M^+).

Anal. Calcd for $C_7H_4NO_2SCl_2F_3$: C, 28.67; H, 1.37; N, 4.78: S, 10.88; Cl, 23.89; F, 19.39. Found: C, 28.55; H, 1.44; N, 4.85; S, 11.15; Cl, 24.00; F, 18.95.

Triflylamide 2a was converted to the oxamide 2 according to the procedure described for 1. Recrystallization from cyclohexane afforded pure 2 (yield, 94%): mp 148-150°C; IR (CH_2Cl_2) 1750, 1730, 1210 and 1130 cm^{-1}; NMR (acetone - D_6) δ 7.7 and δ 7.9 ppm (aromatic protons); mass spectrum (EI), m/e 642 (M^+).

Anal. Calcd for $C_{16}H_6N_2O_6S_2Cl_4F_6$: C, 29.92: H, 0,90; N, 4.36; S.10.00; Cl, 22.12; F, 17.75. Found; C, 30.24; H, 1.02; N, 4.24; S, 10.45; Cl, 22.27; F, 17.19.

N,N'-Bis(2,4,5-trichlorophenyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (3) The trifylamide 3a was prepared according to the procedure described for 1a. Recrystallization of the crude product from cyclohexane afforded pure 3a (yield, 82%): mp 104-106°C; IR(CH_2Cl_2) 3300, 1360, 1210 and 1140 cm^{-1}; NMR ($CDCl_3$) 6.4 (s, 1NH), 7.6 and 7.8 ppm (2s, 2 aromatic protons); mass spectrum (EI), m/e 327 (M^+).

Anal. Calcd for $C_7H_3NO_2SCl_3F_3$: C, 25.69; H, 0.92: N, 4.28; S. 9.79; Cl, 32.11; F, 17.43. Found: C, 25.59; H, 1.00, N, 4.35; S, 9.95; Cl, 31.98; F, 17.00.

The oxamide 3 was prepared from 3a according to the method already described for 1 using methylene chloride as solvent. Recrystallization from methylcyclohexane afforded pure 3 (yield, 78%): mp 190-192°C; IR (CH_2Cl_2) 1750, 1730, 1340, 1210 and 1120 cm^{-1}; NMR (acetone-D_6), δ 7.7 and 7.9 ppm (2s, aromatic protons); mass spectrum (EI), m/e 708 (M^+).

Anal. Calcd for $C_{16}H_4N_2O_6S_2Cl_6F_6$: C, 27.02; H, 0.57; N, 3.94; S, 9.02; Cl, 29.91; F, 16.04. Found: C, 27.02; H, 0.63; N, 3.84; S, 8.90; Cl, 30.06; F, 16.64.

N,N'-Bis(2,4,6-trichlorophenyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (4) Trifylamide 4a was prepared by the procedure already described for 1a. Vacuum sublimation of the crude product afforded pure 4a (yield, 91%): mp 99-101°C; IR (CH_2Cl_2) 3300, 1360 and 1160 cm^{-1}; NMR ($CDCl_3$) δ6.5 (s, 1NH) and 7.8 ppm (s, 2H, 2 aromatic protons); mass spectrum (EI) m/e 327 (M^+).

Anal. Calcd for $C_7H_3NO_2SCl_3F_3$: C, 25.69; H, 0.92; N, 4.28; S, 9.79; Cl, 32.11; F, 17.43. Found: C, 25.52; H, 0.98; N, 4.40; S, 10.01; Cl, 32.15; F, 17.31.

Trifylamide 4a was converted to the oxamide 4 by the procedure described for 1. Recrystallization from cyclohexane afforded pure 4 (yield, 73%): mp 170-172°C IR ($CDCl_3$) 1740, 1380, 1260, 1210 and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.8 ppm (s, 4H aromatic protons); mass spectrum (EI), m/e 708 (M^+).

Anal. Calcd for $C_{16}H_4N_2O_6S_2Cl_6F_6$: C, 27.02; H, 0.57; N, 3.94; S, 9.02; Cl, 29.91; F, 16.04. Found: C, 26.91; H, 0.60; N, 3.80; S, 8.85; Cl, 30.02; F, 16.40.

N,N'-Bis(4-nitrophenyl)-N,N'-Bis(trifluoromethyl sulfonyl) oxamide

The crude trifyl amide 5a (yield, 72%) was prepared by the procedu described for 1a: IR (CH_2Cl_2) 3250, 1350, 1220 and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (s, 1NH) and 7.4 to 7.5 ppm (2s, 4 aromatic proto mass spectrum (EI), m/e 270 (M^+). It was used without further purification in the preparation of the oxamide 5 following the procedure already described for 1. Recrystallizatio from diethyl ether afforded pure 5 (yield, 92%): mp 172-175°C; IR(CH_2Cl_2) 1750, 1730, 1350, 1210 and 1130 cm^{-1}; NMR ($CDCl_3$) δ7.7 to 7.9 ppm (4s, aromatic protons); mass spectrum (EI), m/e 562 (M^+).

Anal. Calcd for $C_{16}H_8N_4O_8S_2F_6$: C, 34.16; H, 1.42; N, 9.96; S, 11.39; F, 20.28. Found: C, 34.46; H, 1.25; N, 9.80; S, 11.78; F, 19.82.

N,N'-Bis(2-methoxyethyl)-N,N'-bis(trifluoromethylsulfonyl) oxamide (6) The trifly amide 6a (yield, 96%) was prepared by the procedure described for 1a. Vacuum distillation afforded pure 6a: bp 50-51°C at .5 mm: IR (liquid) 3300, 3150, 1370, 1250, 1170 and 1120 cm^{-1}; NMR ($CDCl_3$) δ3.5 (s, 3H), 3.7 (s, 4H) and 6.1 (s, 1NH); mass spectrum (CI), m/e 208 $(M+H)^+$.

Anal. Calcd for $C_4H_8NO_3SF_3$: C, 23.19; H, 3.86; N, 6.76; S, 15.46; F, 27.54. Found: C, 22.94; H, 3.73; N, 6.49; S, 15.15; S, 26.95.

The trifyl amide 6a was converted to the oxamide 6 (yield, 99%) by the procedure described for 1. Vacuum distillation afforded pure 6: bp 74-76°C at .5mm; IR (liquid) 1740, 1720, 1420, 1320, 1200, 1160 and 1120 cm^{-1}; NMR ($CDCl_3$) δ3.4 (s, 3H), 3.7 (t, 2H, J = 6Hz) and 4.0 ppm (t, 2H, J=6Hz); mass spectrum (CI m/e 461 $(M + H)^+$.

Anal. Calcd for $C_{10}H_{14}N_2O_8S_2F_6$: C, 25.64; H, 2.99; N, 5.98; S, 13.68; F, 24.36; Found: C, 25.60; H, 3.11; N, 5.77; S, 13.92; F, 23.95.

N,N'-Bis(2-chloroethyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (7) To a suspension of 2-chloroethyl amine hydrochloride (5.80 g; 0.05 mol) and powdered 3A molecular sieves (15g, from Linde Division, Union Carbide Corporation) in dichloroethane (100 mL) was added dropwise trifluoromethanesulfonyl chloride (5.3 mL; 0.025 mol) at room temperature under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at 80°C for 20 hours. Filtration of the solid from reaction mixture, followed by evaporation of the filtrate gave 3.26g (31%) of crude liquid product. Vacuum distillation of the liquid gave pure 2-chloroethyl-trifluoromethylsulfonyl amide 7a: bp 53-55°C at .5mm; IR liquid 3310, 3150, 1420, 1370, 1220, 1200 and 1150 cm^{-1}; mass spectrum (CI), m/e 212 $(M + H)^+$.

Anal. Calcd. for $C_3H_5NO_2SClF_3$: C, 17.06; H, 2.37; N, 6.64; S, 15.17; Cl, 16.59; F, 27.01. Found: C, 17.42; H, 2.51; N, 6.54; S, 15.38; Cl, 16.21; F, 26.79.

Oxalyl chloride (0.58 mL; 0.0067 mol) was added dropwise into a solution of 7a (2.80 g; 0.013 mol) and "Proton Sponge"^{R} (1.44g; 0.0067 mol., from Aldrich Chemical Company, Inc) in methylene chloride (50 mL) at 0°C under a nitrogen atmosphere. After the addition, the mixture was stirred at room temperature for 24 hours. Solvent was evaporated, and the residue was treated with diethyl ether. The ethereal solution was dried

over sodium sulfate. Evaporation of ether followed by the treatment of residue with petroleum ether gave 2.55 g (80%) of crude product. Recrystallization of the crude product from petroleum ether afforded pure 7: mp 71-73°C ; IR (CH_2Cl_2) 1720, 1400, 1360, 1320, 1230, 1160 and 1120 cm^{-1}; mass spectrum (CI), m/e 477 $(M + H)^+$.

Anal. Calcd. for $C_8H_8N_2O_6S_2Cl_2F_6$: C, 20.17; H, 1.68; N, 5.88; S, 13.45; Cl, 14.71; F, 23.95: Found: C, 20.05; H, 1.49; N, 5.92; S, 13.20; Cl, 14.98; F, 23.60.

N,N'-Bis(2-chloro-3-pyridyl)-N,N'-Bis(trifluoromethylsulfonyl) oxamide (8) To a suspension of 2-chloro-3-aminopyridine (5.14g; 0.04 mol) and powdered 3A molecular sieves (10 g) in methylene chloride (60 mL) was added dropwise trifluoromethanesulfonic anhydride (3.4 mL; 0.02 mol) at 0°C under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at room temperature for 5 hours and then the solid was filtered. Filtrate was evaporated and treated with water to give 5.0 g (48%) of crude solid product. It was collected and recrystallized from cyclohexane to give pure 2-chloro-3-pyridyl-trifluoromethylsulfonyl amide 8a: mp120-122°C;IR (CH_2Cl_2) 3300, 1370, 1230, 1210 and 1140 cm^{-1}; NMR ($CDCl_3$) δ7.35 (m. 1H), 8.0 (2d, 1H, J=4HZ), 8.35 (2d, 1H, J=4HZ) and 8.30 ppm (s 1NH); mass spectrum (EI), m/e 260 (M^+).

Anal. Calcd for $C_6H_4N_2O_2SClF_3$: C, 27.69; H, 1.54; N, 10.77; S, 12.31; Cl, 13.46; F, 21.92. Found: C, 27.85, H, 1.41; N, 11.00; S, 11.95; Cl, 13.66; F, 21.50.

Oxalyl chloride (0.53 mL; 0.006 mol) was added dropwise into a stirring suspension of 8a (2.61 g; 0.01 mol) and powdered 3A molecular sieves (5.0g) in methylene chloride (75 mL) at 0°C under a nitrogen atmosphere. The mixture was then heated to 60°C, held thereat for 3 hours, and then at room temperature for 60 hours. The reaction mixture was filtered and the filtrate was evaporated to dryness. The resulting residue was extracted with diethyl ether, and the combined ethereal extracts were dried over sodium sulfate. Evaporation of the dried ethereal solution obtained 2.33 g (81%) of crude product. Recrystallization of the crude product from cyclohexane gave pure 8: mp 104-106°; IR (CH_2Cl_2) 1750, 1730, 1420, 1360, 1220 and 1130 cm^{-1}; NMR ($CDCl_3$) δ 7.50 (m, 1H), 8.10 (2d, 1H, J=4HZ), and 8.5 ppm (m, 1H); mass spectrum (EI), m/e 574 (M^+).

Anal. Calcd. for $C_{14}H_6N_2O_6S_2Cl_2F_6$: C, 29.27; H, 1.05; N, 9.76; S, 11.15; Cl, 12.20; F, 19.86. Found: C, 29.10; H, 1.14; N, 9.90; S, 10.89; Cl, 11.95; F, 19.40.

References and Notes

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(b) Presented in part at the 178th ACS National Meeting, Washington, D.C., September, 1979.

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TABLE I

CHEMILUMINESCENCE PERFORMANCE OF N-TRIFYL OXAMIDES[a],

$F_3CO_2SN(R)COCO\ N(R)SO_2CF_3$

COMPOUND R =	CONC M	Q.Y.[b] x 10^{-2}	Mean Q.Y.	T.75[c] min.	Light Capacity[d]
1 4 -chlorophenyl	.01	11.4		44.9	37.5
2 2,4-dichlorophenyl	.01	26.2		139	85.0
	.01	25.6	25.9	116	85.4
3 2,4,5-trichlorophenyl	.01	32.6		50.4	108
	.01	35.4	34.0	42.3	117
4 2,4,6-trichlorophenyl	.01	11.4		100	37.8
	.01	13.6	12.5	82.9	45.0
5 4-nitrophenyl	.01	11.0		8.88	35.7
6 2-methoxyethyl	.01	2.85		70.2	9.20
7 2-chloroethyl	.01	3.68		125	12.2
8 2-chloro-3-pyridyl	.008	15.5		129	41.3

[a]Chemiluminescent reactions contained the indicated concentrations of the oxamide, 6.75×10^{-3}M 1-chloro-9,10-bis(phenylethynyl)anthracene, .375M hydrogen peroxide and 3×10^{-4}M sodium salicylate in a solvent mixture of 75% (by volume) dibutylphthalate, 20% dimethyl phthalate, 5% t-butanol.

[b]Chemiluminescent quantum yield in einsteins per mole of oxamide.

[c]Time required for 75% of the total light to be emitted.

[d]Integrated visible light output in lumen-hours per liter.

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